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• Tabler, Raymond Lee
Midland, Michigan (US)
• Homan, Gary Rex
Midland, Michigan (US)

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(71) Applicant: DOW CORNING CORPORATION
Midland, Michigan 48686-0994 (US)

(74) Representative: Vandamme, Luc Johan Roger
Dow Corning Limited,
Cardiff Road
Barry, South Glamorgan CF63 2YL, Wales (GB)

(72) Inventors:

• Chung, Kyuha
Midland, Michigan (US)

(54) Aerosol suppressant compositions for silicone coatings

(57) Disclosed herein is a method of preparing an aerosol suppressant composition and the use of said composition to reduce silicone mist in high speed coating processes which also significantly increases the adhesion of the coating to the substrate. The method comprises preparing an aerosol suppressant composition by reaction of an organosilicon compound, an oxyalkylene containing compound and a catalyst. The composition, when added to curable silicone coatings, thereby reduces the amount of silicone mist in high speed coating processes.

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Description

The present invention relates to a method of preparing an aerosol suppressant composition and to the use of said composition in silicone coatings to reduce or suppress silicone mist produced in high speed coating processes which also significantly increases the adhesion of the coating to the substrate. Said method prepares the aerosol suppressant composition by reacting a mixture of an organosilicon compound, an oxyalkylene containing compound and a catalyst. This invention also relates to the use of aerosol suppressant compositions in processes for preparing a laminate of a substrate and an adhesive, wherein the adhesive will release from the substrate.

A current trend in the silicone coating industry is to operate coating machinery as fast as possible to increase productivity. As silicone materials are applied to a substrate at very high speeds such as 304.8 to 457.2 m/min (1000 to 1500 ft/min), the coating material tends to form a "mist" which comprises very fine particles blown out from the coating head. Recently this phenomenon has become one of the most serious problems in the industry. Although the coating materials are capable of fast thermal cure or are even radiation curable, presently they cannot be coated at high speed due to the misting problem.

Another trend in the silicone coating industry is to use plastic films, such as polyolefins and polyesters, as a substrate for the curable coating which requires that the silicone coating anchor to the plastic film. In the past, good film anchorage has required curing at higher temperatures and at slow curing rates. Thus, fast cure formulations could not be applied to plastic films due to the aforementioned problems. Furthermore, since plastic films cannot tolerate high temperatures during the coating process only very limited applications exist which can employ those films as substrates for coatings.

20 The present invention is directed at solving these problems.

Organosilicon compounds containing oxyalkylene (functionality) are generally represented by the following patent publications: GB-A 0981811; US-A 3,478,075; US-A 4,025,456; US-A 4,847,398 and US-A 4,857,583. Likewise, silicone compounds suitable as defogging compositions or as anti-misting agents are specifically disclosed in US-A 4,567,221; JP-A 23748/1977, 27495/1978, 27496/1978 and 27497/1978.

25 However, none of these references discloses a method of preparing an aerosol suppressant composition comprising reacting an organosilicon compound, an oxyalkylene containing compound, and a catalyst which, when added to curable silicone coatings, reduces the amount of mist in high speed coating processes.

The present invention introduces a method of making an aerosol suppressant composition, the method comprising the steps of: (i) reacting a mixture of: (A) an organosilicon compound selected from the group consisting of (i) an organohydrogensilicon compound, (ii) an organosilicon compound having in the compound at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy groups, amine groups, hydroxyl groups, alkoxy groups, carboxyl groups, isocyanate groups, oxime groups, acetoxy groups, and mixtures thereof, and (iii) mixtures of (i) and (ii); (B) a compound having its formula selected from the group consisting of: $RO-(R^1O)_x(R^2O)_yR$, $RO-(R^1O)_xR$, and $RO-(R^2O)_yR$, wherein R is selected from hydrogen atom or an olefinic hydrocarbon radical having from 3 to 14 carbon atoms, R¹ and R² are alkylene radicals having from 2 to 4 carbon atoms with the proviso that R¹ and R² are not the same alkylene radical at any given time, x has a value of from 1 to 200, y has a value of from 1 to 200, with the proviso that R is the same on both molecular chain ends; and (C) a catalyst selected from metal catalysts or complexes of metal catalysts, in a sufficient amount to form a reaction product.

30 The present invention comprises reacting organosilicon compound (A), compound (B) and compound (C). The organosilicon compound (A) is (i) an organohydrogensilicon compound. This compound is preferably free of aliphatic unsaturation and contains two or more silicon atoms linked by divalent radicals, an average of from one to two silicon-bonded monovalent radicals per silicon atom and an average of at least one, and preferably two, three or more silicon-bonded hydrogen atoms per molecule. Preferably, the organohydrogensiloxane contains an average of three or more silicon-bonded hydrogen atoms such as, for example, 5, 10, 20, 40, 70, 100 and more. The organohydrogensiloxane compounds suitable as compound (A) are linear, branched, cyclic, resins, and combinations thereof.

35 Highly preferred linear organohydrogenpolysiloxanes as (A)(i) have the formula $YMe_2SiO(Me_2SiO)_p(MeY-SiO)_qSiMe_2Y$ wherein Me denotes methyl, and Y denotes hydrogen atom or methyl. An average of at least two Y radicals per compound must be hydrogen atoms. The subscripts p and q have average values of zero or more and the sum of p plus q has a value ranging from 0 to 1000. The disclosure of US-A 4,154,714 teaches highly-preferred organohydrogenpolysiloxanes.

40 Especially preferred as compound (A)(i) are methylhydrogensiloxanes selected from the group consisting of bis(trimethylsiloxy)dimethylidihydrogendisiloxane, heptamethylhydrogentrisiloxane, hexamethylidihydrogentrisiloxane, methylhydrogencyclosiloxanes, pentamethylpentahydrogencyclopentasiloxane, pentamethylhydrogendisiloxane, polymethylhydrogensiloxanes, tetramethyltetrahydrogencycloctetrasiloxane, tetramethylidihydrogenidisiloxane, and methylhydrogendimethylsiloxane copolymers such as dimethylhydrogensiloxy terminated methylhydrogendimethylsiloxane copolymers.

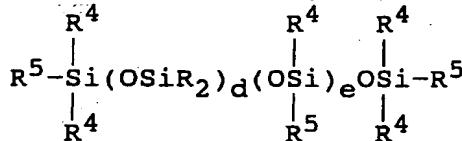
45 The organosilicon compound (A) is also (ii) an organosilicon compound having at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy groups, amine groups, hydroxyl groups, alkoxy groups, carboxyl groups, isocyanate groups and mixtures thereof.

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The olefinic hydrocarbon radicals of (A) (ii) have from 2 to 14 carbon atoms. The olefinic hydrocarbon radicals are preferably selected from the group consisting of the vinyl radical and higher alkenyl radicals represented by the formula $-R^3(CH_2)_rCH=CH_2$ wherein R^3 denotes $-(CH_2)_s-$ or $-(CH_2)_tCH=CH-$ and r has the value of 1, 2, or 3, s has the value of 0 to 9, and t has the value of 3, 4 or 5. The higher alkenyl radicals represented by the formula $-R^3(CH_2)_sCH=CH_2$ contain at least 6 carbon atoms. For example, when R^3 denotes $-(CH_2)_s-$, the higher alkenyl radicals include 5-hexenyl, 6-heptenyl, 7-octenyl, 8-nonenyl, 9-deceny, and 10-undecenyl. When R^3 denotes $-(CH_2)_tCH=CH-$, the higher alkenyl radicals include 4,7-octadienyl, 5,8-nonadienyl, 5,9-decadienyl, 6,11-dodecadienyl and 4,8-nonadienyl. Alkenyl radicals selected from the group consisting of 5-hexenyl, 7-octenyl, 9-deceny and 5,9-decadienyl are preferred. It is more preferred that R^3 denote $-(CH_2)_s-$ so the radicals contain only terminal unsaturation and the most preferred radicals are the vinyl radical and the 5-hexenyl radical.

Specific examples of preferred olefinic hydrocarbon containing polydiorganosiloxanes for use as organosilicon compound (A)(ii) include $ViMe_2SiO(Me_2SiO)_aSiMe_2Vi$, $HexMe_2SiO(Me_2SiO)_aSiMe_2Hex$, $Vi_2MeSiO(Me_2SiO)_aSiMeVi_2$, $Hex_2MeSiO(Me_2SiO)_aSiMeHex_2$, $Vi_3SiO(Me_2SiO)_aSiVi_3$, $Hex_3SiO(Me_2SiO)_aSiHex_3$, $PhMeViSiO(Me_2SiO)_aSiPhMeVi$, $HexMe_2SiO(Me_2SiO)_a(MeHexSiO)_bSiMe_2Hex$, $ViMe_2SiO(Me_2SiO)_a(MeViSiO)_bSiMe_2Vi$, $Hex_2MeSiO(Me_2SiO)_a(MeH-exSiO)_bSiMeHex_2$, $Vi_2MeSiO(Me_2SiO)_a(MeViSiO)_bSiMeVi_2$, $Hex_3SiO(Me_2SiO)_a(MeHexSiO)_bSiHex_3$, $Vi_3SiO(Me_2SiO)_a(MeViSiO)_bSiVi_3$, wherein Me , Vi , Hex and Ph denote methyl, vinyl, 5-hexenyl and phenyl, respectively. "a" has a value of 0 to 500 and b has value of 0 to 200.

The organosilicon compound (A)(ii) is also an organosilicon compound having at least one vinyl ether group in the molecule. The vinyl ether groups are bonded to silicon via SiC or $SiOC$ bonds. Organosilicon compounds having vinyl ether groups attached to silicon via SiC bonds are exemplified by compounds disclosed in US-A 4,617,238; US-A 5,057,549; EP-A 0462389; CA 2,035,369; US-A 5,145,915 and PCT 93/022369. These publications teach SiC -bonded vinyl ether containing organopolysiloxanes also suitable as our organosilicon compound (A)(ii). Particularly preferred as the SiC -bonded vinyl ether containing organosilicon compounds are the vinyl ether functional organopolysiloxanes having the formula



wherein R^4 is a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms or an alkoxy radical having from 1 to 8 carbon atoms, R^5 is R^4 or a group having its formula selected from the group consisting of

- (a) $-(CH_2)_n(OR^6)_cOCH=CH_2$ or
- (b) $(H_2C=CHOR^6)_zCR^7_{4-z}(OR^6)_c(CH_2)_n-$

wherein R^6 is a divalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms, R^7 is a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms or hydrogen atom, and z has a value of 1 or 2, d has a value from 0 to 500, and e has a value from 0 to 200, c has a value of 0 to 10, and n has a value of from 1 to 20, with the proviso that at least one group having its formula selected from the group consisting of

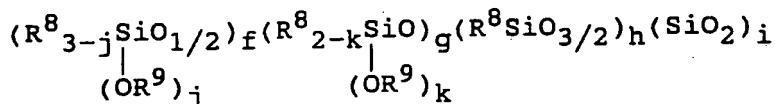
- (a) $-(CH_2)_n(OR^6)_cOCH=CH_2$ or
- (b) $(H_2C=CHOR^6)_zCR^7_{4-z}(OR^6)_c(CH_2)_n-$

is present in the molecule.

The monovalent radicals of R^4 contain up to 20 carbon atoms and include halohydrocarbon radicals free of aliphatic unsaturation and hydrocarbon radicals. Monovalent hydrocarbon radicals include alkyl radicals, such as methyl, ethyl, propyl, butyl, hexyl, octyl and decyl; cycloaliphatic radicals, such as cyclohexyl; aryl radicals, such as phenyl, tolyl and xylyl; and aralkyl radicals, such as benzyl or phenylethyl. Highly preferred monovalent hydrocarbon radicals for R are methyl or phenyl. Monovalent halohydrocarbon radicals free of aliphatic unsaturation include any monovalent hydrocarbon radical noted above which is free of aliphatic unsaturation and which has at least one of its hydrogen atoms replaced with a halogen, such as fluorine, chlorine or bromine. The several R radicals are identical or different, as desired, and preferably at least 50 percent of all R radicals are methyl.

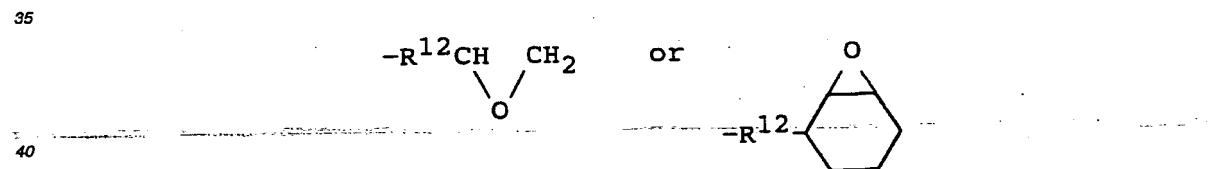
The group R⁶ is a divalent hydrocarbon group having from 1 to 20 carbon atoms which is exemplified by groups such as alkylene radicals including methylene, ethylene, propylene, butylene, phenylene, trimethylene, 2-methyltrimethylene, pentamethylene, hexamethylene, 3-ethyl-hexamethylene, octamethylene, -CH₂(CH₃)CH-, -CH₂CH(CH₃)CH₂- and -(CH₂)₁₈-; cycloalkylene radicals such as cyclohexylene; arylene radicals such as phenylene; combinations of divalent hydrocarbon radicals such as benzylene (-C₆H₄CH₂-); hydroxylated hydrocarbon residues; chloroethylene; fluorooethylene; -CH₂CH₂OCH₂-; -CH₂CH₂OCH₂CH₂-; -CH₂CH₂OCH(CH₃)CH₂- and -CH₂OCH₂CH₂OCH₂CH₂-.

Organosilicon compounds having vinyl ether groups attached to silicon via SiOC bonds are disclosed in US-A 5,270,423 which discloses representative SiOC-bonded vinyl ether organopolysiloxanes that are suitable as organosilicon compound (A)(ii). Particularly preferred as the SiOC-bonded vinyl ether containing organosilicon compound are the vinyl ether functional organopolysiloxanes having the general formula



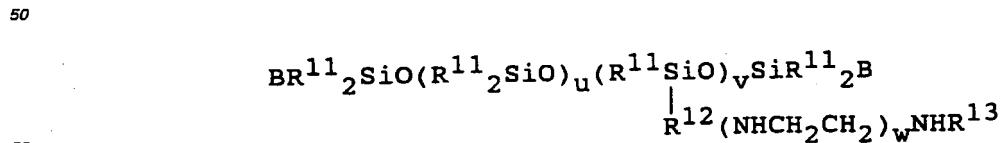
wherein R⁸ is a monovalent hydrocarbon radical or halo hydrocarbon radical having from 1 to 20 carbon atoms as delineated above, R⁹ is selected from the group consisting of monovalent hydrocarbon or halo hydrocarbon radicals having from 1 to 8 carbon atoms and a group having its formula selected from the group consisting of (i) -R¹⁰OCH=CH₂ or (ii) -R¹⁰Si[OR¹⁰OCH=CH₂]_{3-m}R⁸_m wherein R¹⁰ is a divalent hydrocarbon or halo hydrocarbon radical having from 1 to 20 carbon atoms as delineated above, m has a value of 0 to 2, R⁸ is as defined above, f has a mole percent of from greater than 0 to 100, g has a mole percent of from 0 to less than 100, h has a mole percent of from 0 to less than 100, i has a mole percent of from 0 to less than 100, j is an integer of from 0 to 3, k is an integer of from 0 to 2, the sum of f+g+h+i is equal to 100 mole percent, with the proviso that at least one =SiOR¹⁰OCH=CH₂ group or =SiOR¹⁰Si[OR¹⁰OCH=CH₂]_{3-m}R⁸_m group exists in each molecule. These compounds are further described in copending application EP-A 0625535 which is commonly assigned to the same assignee as the present application.

The organosilicon compound (A)(ii) is also an organosilicon compound having at least one epoxy group in the molecule. Preferred as this (A)(ii) are the epoxy functional organopolysiloxanes having the general formula AR¹¹₂SiO(R¹¹₂SiO)_u(R¹¹ESiO)_vSiR¹¹₂A wherein R¹¹ is a monovalent hydrocarbon radical having from 1 to 20 carbon atoms as delineated above, E is an epoxy group having its formula selected from



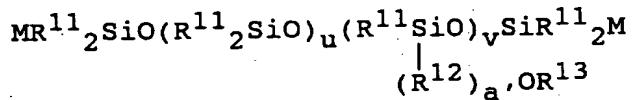
wherein R¹² is a divalent hydrocarbon group having from 1 to 20 carbon atoms as delineated above, A denotes R or E, u has a value of 0 to 500, v has a value of 0 to 200 with the proviso that there are at least two epoxy groups per compound. The preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

The organosilicon compound (A)(ii) is also an organosilicon compound having at least one amine group in the molecule. Preferred as this (A)(ii) are the amino functional organopolysiloxanes having the general formula:



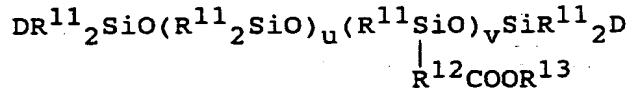
wherein R¹¹ and R¹² are as defined above, R¹³ denotes hydrogen atom or R¹¹, w has a value of 0 to 10, B denotes R¹¹ or -R¹²(NHCH₂CH₂)_wNHR¹³, u and v are as defined above, with the proviso that there are at least two -R¹²(NHCH₂CH₂)_wNHR¹³ groups per molecule. The preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

5 The organosilicon compound (A)(ii) is also an organosilicon compound having at least one hydroxyl group or alkoxy group in the molecule. Preferred hydroxy and alkoxy functional organopolysiloxanes have the general formula



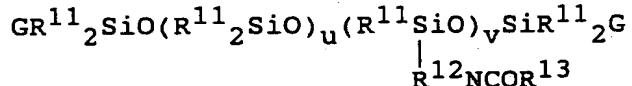
15 wherein R¹¹, R¹² and R¹³ are as defined above, a' has a value of 0 or 1, M denotes R¹¹ or -(R¹²)_aOR¹³, u and v are as defined above, with the proviso that there are at least two -OR¹³ groups per molecule. Preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

20 The organosilicon compound (A)(ii) is also an organosilicon compound having at least one carboxyl group in the molecule. Preferred carboxyl functional organopolysiloxanes have the general formula



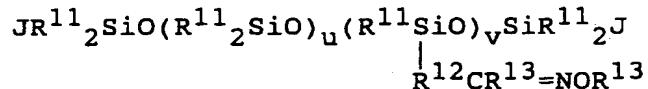
30 wherein R¹¹, R¹² and R¹³ are as defined above, D denotes R¹¹ or -R¹²COOR¹³, u and v are as described hereinabove, with the proviso that there are at least two -R¹²COOR¹³ groups per molecule. Preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

35 The organosilicon compound (A)(ii) is also an organosilicon compound having at least one isocyanate group in the molecule. Preferred as this (A)(ii) are the isocyanate functional organopolysiloxanes having the general formula:



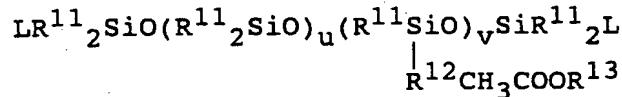
45 wherein R¹¹, R¹² and R¹³ are as defined above, G denotes R¹¹ or -R¹²NCOR¹³, u and v are as defined above, with the proviso that there are at least two -R¹²NCOR¹³ groups per molecule. The preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

50 The organosilicon compound (A)(ii) is also an organosilicon compound having at least one oxime group in the molecule. Preferred as this (A)(ii) are the oxime functional organopolysiloxanes having the general formula:



wherein R¹¹, R¹² and R¹³ are as defined above, J denotes R¹¹ or -R¹²CR¹³=NOR¹³, u and v are as defined above, with the proviso that there are at least two -R¹²CR¹³=NOR¹³ groups per molecule. The preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

The organosilicon compound (A)(ii) is also an organosilicon compound having at least one acetoxy group in the molecule. Preferred as this (A)(ii) are the acetoxy functional organopolysiloxanes having the general formula:



wherein R₁₁, R₁₂ and R₁₃ are as defined above, L denotes R₁₁ or -R₁₂CH₃COOR₁₃, u and v are as defined above, with the proviso that there are at least two -R₁₂CH₃COOR₁₃ groups per molecule. Preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

The organosilicon compound suitable as (A)(ii) is also an organosilicon compound having a mixture of any of the groups denoted above for (A)(ii), such as an organosilicon compound having amino groups and isocyanate groups; an organosilicon compound having amino, carboxyl and alkoxy groups; an organosilicon compound having olefinic hydrocarbon groups and alkoxy or hydroxy groups.

The organosilicon compound (A) is also a mixture of organosilicon compounds (i) and (ii) delineated above, i.e. a mixture of the organohydrogensilicon compound (i) and the organosilicon compound having at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy groups, amine groups, hydroxyl groups, alkoxy groups, carboxyl groups, isocyanate groups, oxime groups, acetoxy groups or mixtures of (A)(ii).

The olefinic hydrocarbon radicals suitable as R in compound (B) are as delineated for compound (A) including preferred embodiments thereof. Highly preferred olefinic hydrocarbon radicals for (B) include the vinyl and the 5-hexenyl radicals. The group R is the same on both molecular chain ends of compound (B), i.e. the R group must be identical on both ends of the chain. Thus, if R is hydrogen atom on one end of compound (B), then R must be hydrogen atom on the other end of compound (B).

The groups R¹ and R² in compound (B) are alkylene radicals having from 2 to 4 carbon atoms. Thus, R¹ and R² are selected from the group consisting of ethylene, propylene, butylene, isopropylene and isobutylene. The groups R¹ and R² are preferably selected from ethylene, isopropylene or a mixture thereof. The groups R¹ and R² are not the same alkylene radical at any given time. In compound (B), x has a value of from 1 to 200 and y has a value of from 1 to 200. It is also preferred that x have a value from 10 to 100, and y have a value from 1 to 100. It is also preferred that when compound (B) is an ethylene-isopropylene copolymer, that the value of x+y is from 10 to 40. When R¹ is ethylene only, the value of x is from 10 to 20 and when R¹ is isopropylene only, the value of x is from 25 to 40.

Groups suitable as compound (B) include compounds having their formula selected from the group consisting of $\text{H}_2\text{C}=\text{CH}-(\text{CH}_2)_{b'}-\text{O}-(\text{C}_2\text{H}_4\text{O})_x-(\text{C}_3\text{H}_6\text{O})_y-(\text{CH}_2)_{b'}-\text{CH}=\text{CH}_2$, $\text{CH}_3-\text{CH}=\text{CH}-(\text{CH}_2)_{b'}-\text{O}-(\text{C}_2\text{H}_4\text{O})_x-(\text{C}_3\text{H}_6\text{O})_y-(\text{CH}_2)_{b'}-\text{CH}=\text{CH}-\text{CH}_3$, and $\text{HO}-(\text{C}_2\text{H}_4\text{O})_x-(\text{C}_3\text{H}_6\text{O})_y-\text{H}$ wherein b' has a value of 1 or greater than 1, the value of b' being the same or different as desired, x has a value of 0 to 200, and y has a value of 0 to 200 with the proviso that the value of $x+y$ is at least 1.

40 The amount of compound (B) varies depending on the amount of compound (A) and catalyst (C) that is employed. It is preferred that from 5 to 2000 weight parts of compound (B) be used per 100 weight parts of (A), and it is highly preferred that from 5 to 20 weight parts of compound (B) be employed per 100 weight parts of compound (A).

Catalyst (C) is a metal catalyst or a complex of a metal catalyst. Preferably, metal catalyst (C) is selected from the group consisting of potassium, lithium, tin, titanium, calcium, sodium, platinum and rhodium metal catalysts and complexes thereof. Metal catalysts include the Group VIII metal catalysts and complexes thereof. By Group VIII metal catalysts, it is meant iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The metal catalyst (C) can be a platinum containing catalyst compound since they are the most widely used and available. Platinum-containing catalysts are platinum metal, optionally deposited on a carrier such as silica gel or powdered charcoal; or a compound or complex of a platinum group metal.

50 A preferred platinum-containing catalyst is a form of chloroplatinic acid, either as the commonly available hexahydrate form or as the anhydrous form, as taught by US-A 2,823,218. A particularly useful catalyst is that composition obtained when chloroplatinic acid is reacted with an aliphatically unsaturated organosilicon compound, such as divinyltetramethyldisiloxane, as disclosed in US-A 3,419,593, because of its easy dispersibility in organosilicon systems. Other Group VIII metal catalysts suitable as (C) include RhCl_3 , RhBr_3 , and Rhl_3 and complexes thereof; $\text{CIRh}(\text{PPh}_3)_3$ and complexes thereof; H_2PtCl_6 ; a complex of 1,3-divinyl tetramethyl disiloxane and H_2PtCl_6 ; and alkyne complexes of H_2PtCl_6 .

Potassium, lithium and sodium catalysts as metal catalyst (C) includes hydroxides, silanlates, alcoholates, siloxanlates and mercaptides of the Group IA alkali metals.

Potassium catalysts suitable as metal catalyst (C) include potassium hydroxide, potassium silanolate, potassium alcoholate, potassium phenolate, potassium siloxanolate, potassium mercaptide and potassium polyethers.

Lithium catalysts suitable as metal catalyst (C) include lithium hydroxide, lithium alcoholate, lithium silanolate, lithium siloxanolate, lithium phenolate, lithium mercaptide, anhydrous lithium hydroxide and lithium polyethers.

Sodium catalysts suitable as metal catalyst (C) include sodium hydroxide, sodium alcoholate, sodium phenolate, sodium silanolate, sodium siloxanolate and sodium mercaptide.

Tin catalysts suitable as metal catalyst (C) include organotin compounds such as dibutyltin dilaurate, dibutyltin dioctoate, stannous acetate, stannous octoate, stannous benzoate, stannous sebacate, stannous succinate, tin octoate, dibutyltin diacetate and stannous naphthanate.

Titanium catalysts suitable as metal catalyst (C) include organotitanates such as tetraisopropyl titanate, tetrabutyl titanate, tetraethylhexyl titanate, tetraphenyltitanate, triethanolamine titanate, titanium naphthanate, siloxytitanates such as tetrakis(trimethylsiloxy)titanium and bis(trimethylsiloxy)-bis(isopropoxy)titanium and betadicarbonyltitanium compounds such as bis(acetylacetonyl) diisopropyl titanate.

The metal catalyst (C) can be diluted with a solvent prior to adding it to the mixture of step (I). Examples of suitable solvents are aliphatic hydrocarbons such as pentane, hexane, heptane, octane and nonane or aromatic hydrocarbons such as benzene, toluene and xylene. The amount of solvent used with the metal catalyst is not critical and is readily determined by one skilled in the art using routine experimentation. However, it is preferred that catalyst be diluted with from 90 parts of solvent per 10 parts of catalyst to as much as 99 parts of solvent per 1 part of catalyst. When a solvent is used with the metal catalyst (C), it may be necessary to strip off the solvent after the formation of the reaction product.

Methods of stripping volatile components are well-known in the art and need no extensive delineation herein. Thus, volatile components are removed by molecular stills, rotoevaporators and wipe film evaporators, with the preferred method being rotoevaporators.

The most effective concentration of metal catalyst ranges from 0.01 to 1 weight part per 100 parts of compound (A), and it is highly preferred that from 0.01 to 0.20 weight parts per 100 parts of (A) be employed.

When component (A) is organohydrogensilicon compound (I), the reaction mixture of (I) can further comprise an organic compound having at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy groups, amine groups, isocyanate groups, oxime groups, acetoxy groups and mixtures thereof.

Examples of organic compounds containing olefinic hydrocarbon radicals include dienes such as 1,3 hexadiene, 1,5 hexadiene, 1,4 hexadiene, 2,4 hexadiene, propadiene, 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,6-heptadiene, 1,7-octadiene and 1,9-decadiene.

Examples of organic compounds containing vinyl ether groups include hydroxybutylvinylether, hydroxypropylvinylether, p-phenolvinylether, hydroxybutyl-2-methylvinylether or $H(O(CH_2)_2)_3-OCH=CH_2$.

Examples of organic compounds containing epoxy groups include organic epoxides including vinyl or allyl functional epoxides such as 1,2-epoxy-5-hexene, 3,4-epoxy-1-butene, 5,6-epoxy-1-hexene, 7,8-epoxy-1-octene, 11,12-epoxy-1-dodecene, allyl glycidyl ether, 1-methyl-4-isopropenyl cyclohexeneoxide, 1,4-dimethyl-4-vinylcyclohexeneoxide and 2,6-dimethyl-2,3-epoxy-7-octene.

Examples of organic compounds containing isocyanate groups include unsaturated isocyanates such as allyl isocyanate.

Examples of organic compounds containing amine groups include compounds such as 2-amino-2-methyl-propanol. It is preferred that from 5 to 200 weight parts of organic compound per 100 parts of compound (A) be employed, and it is highly preferred that from 20 to 100 weight parts per 100 parts of (A) be employed.

The reaction mixture of (I) can further comprise a foam control agent. Preferably, the foam control agent is a fluorosilicone polymer. Preferred are the compounds claimed in US-A 4,968,766, which shows fluorosilicone polymers suitable as our foam control agent. Preferred as the foam control agent is a fluorosilicone polymer having the general formula $QMe_2SiO(Me_2SiO)_c(TXMeSiO)_d(MeQSiO)_eSiMe_2Q$ wherein Q denotes an alkenyl radical, Me denotes a methyl radical, TX denotes a silicon-bonded fluorinated radical wherein T denotes a perfluoroalkyl radical having from 4 to 16 carbon atoms, X denotes an alkylene radical linking T to Si through at least 2 carbon atoms, wherein the values of c', d', and e' are such that the fluorosilicone polymer contains at least 5 mole percent $(TX)MeSiO_{1/2}$ siloxane units, and from 0.1 to 10 mole percent alkenyl radical-containing siloxane units. Q denotes an alkenyl radical such as vinyl, allyl, butenyl, pentenyl, hexenyl, octenyl and decenyl. Examples of suitable T groups include C_4F_9 -, C_5F_{11} -, C_6F_{13} -, C_7F_{15} -, and C_8F_{17} -, which are further exemplified by groups such as $CF_3CF_2CF_2CF_2$ -, $(CF_3)_2CFCF_2$ -, $(CF_3)C$ -, $CF_3CF_2(CF_3)CF$ -, $CF_3CF_2CF_2CF_2CF_2$ -, $CF_3(CF_2)_4CF_2$ and $CF_3(CF_2CF_2)_3$ -. Examples of suitable X groups are $-CH_2CH_2$ -, $-CH_2CH_2CH_2$ -, $-CH(CH_3)CH_2$ -, $-(CH_2CH_2)_2$ -, $-CH(CH_3)CH_2CH_2$ and $-CH_2(CH_3)CHCH_2$ -. Preferably, TX denotes the group $CF_3CF_2CF_2CF_2CH_2CH_2$ -. In the above formula, c' and e' have a value as small as zero, but d' must have a value of at least one. Preferably, $c'+d'+e'$ has a value of 2500, d' has a value of 750 and e' has a value of 12.5.

It is preferred that from 0.01 to 5 weight parts of foam control agent be employed per 100 parts of compound (A). It is highly preferred that from 0.01 to 0.1 weight parts per 100 parts of (A) be used.

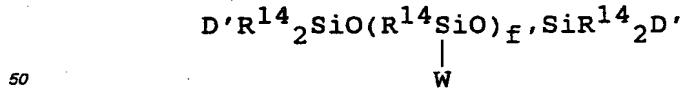
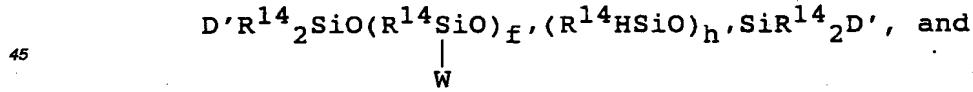
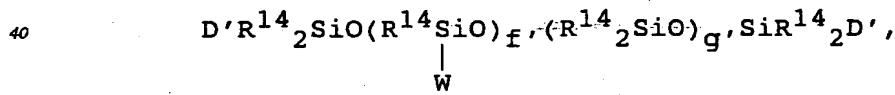
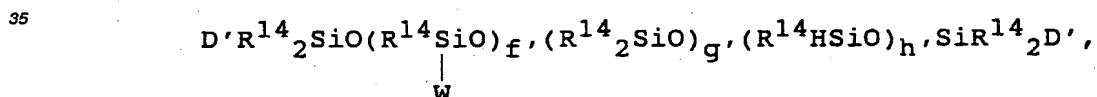
The method of the present invention can further comprise neutralizing the reaction product of step (I). Methods of neutralizing solutions are well known in the chemical arts and need no extensive delineation herein. Neutralization of the reaction product of step (I) is accomplished by adding a compound such as acetic acid, chlorosilanes and carbon dioxide, to the reaction product in an amount sufficient to render the solution neutral (i.e. attain a pH of close to 7). It is highly preferred that when a basic catalyst is employed as catalyst (C), the reaction product of step (I) be neutralized. Preferably, the neutralizing compounds are added in a range of 0.01 to 1 weight parts per 100 weight parts of the reaction product of (I).

5 The method of the present invention can further comprise filtering the reaction product of (I). "Filtration" denotes the separating of suspended solids from a liquid by forcing the mixture through a porous barrier. Methods of filtering 10 solutions are well known in the chemical arts and need no extensive delineation herein. Filtration herein is accomplished by employing filters such as gravity filters, pressure filters, vacuum filters or suction filters. It is highly preferred that when catalyst (C) is a platinum-containing catalyst, the reaction product of (I) is filtered.

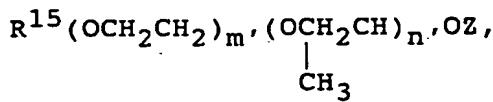
15 The reaction mixture of (I) can further comprise a monohydric alcohol (an alcohol having 1 OH group) having from 1 to 30 carbon atoms. Preferably the alcohol is an alcohol containing olefinic unsaturation. The alcohols are preferably 20 monohydric alcohols such as aliphatic, alicyclic, aromatic, heterocyclic or polycyclic alcohols. Alcohols suitable for use include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 1-hexanol, 1-heptanol, phenol, benzyl alcohol, 1-octanol, 1-nonanol, 1-decanol, undecylenyl alcohol, 2,4-dichlorobenzyl alcohol, phenethyl alcohol, 1-undecanol, 2-methylbenzyl alcohol, 3-methylbenzyl alcohol, 2-phenyl-1-propanol, stearyl alcohol, furfuryl alcohol, tetrahydrofurfuryl alcohol, sterols, cyclohexanol, allyl alcohol ($\text{CH}_2=\text{CHCH}_2\text{OH}$), crotyl alcohol ($\text{CH}_3\text{CH}=\text{CHCH}_2\text{OH}$), methylvinylcarbinol 25 ($\text{CH}_2=\text{CHCH}(\text{OH})\text{CH}_3$), cinnamyl ($\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$), 5-decen-1-ol ($\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_4\text{OH}$), 9-decen-1-ol ($\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_8\text{OH}$), 2-methyl-3-buten-1-ol ($\text{H}_2\text{C}=\text{CHCH}(\text{CH}_3)\text{CH}_2\text{OH}$), 2-methyl-3-buten-2-ol ($\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)_2\text{OH}$), 3-methyl-2-buten-1-ol ($(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{OH}$), 3-methyl-3-buten-1-ol ($\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{OH}$), 2-propenylphenyl ($\text{CH}_3\text{CH}=\text{CHC}_6\text{H}_4\text{OH}$), 1-octen-3-ol ($\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{OH})\text{CH}=\text{CH}_2$), 7-dodecen-1-ol ($\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_6\text{OH}$), 7-tetradecen-1-ol ($\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CH}(\text{CH}_2)_6\text{OH}$), 9-tetradecen-1-ol ($\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_8\text{OH}$), 11-tetradecen-1-ol 30 ($\text{C}_2\text{H}_5\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{OH}$), 11-hexadecen-1-ol ($\text{CH}_3(\text{CH}_2)_3\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{OH}$), and oleyl alcohol ($\text{HO}-(\text{CH}_2)_8\text{CH}=\text{CH}(\text{CH}_2)_7\text{CH}_3$). It is preferred that the alcohol is an unsaturated monohydric alcohol having greater than 10 carbon atoms in its molecular chain.

The amount of alcohol employed varies depending on the amounts of components (A), (B), and (C) that are employed. It is preferred that from 0 to 50 weight parts of alcohol be used, and it is highly preferred that from 5 to 25 35 weight parts be employed, said weight parts being based on 100 parts of compound (A).

The method of the present invention can further comprise adding, after step (I), a silicone glycol copolymer having its general formula selected from the group consisting of



wherein R^{14} is a monovalent hydrocarbon radical having from 1 to 10 carbon atoms, D' is R^{14} or W , f has a value of 1 to 20, g has a value of 1 to 200, h has a value of 1 to 200, W is a polyoxyalkylene group having its average structure selected from



10 R¹⁵(OCH₂CH₂)_mOZ, or



20 wherein R¹⁵ is selected from a divalent hydrocarbon group having 1 to 20 carbon atoms or a urethane group, m' has a value of 1 to 50, n' has a value of 1 to 50, and Z is selected from the group consisting of hydrogen atom, an alkyl radical having 1 to 6 carbon atoms and an acyl group having 2 to 6 carbon atoms with the proviso that the value of m'+n' is greater than 5. It is preferred that f' is between 1 and 10, g' is between 1 and 100, m' is between 1 and 25, and n' has a value of 1 to 50. The monovalent hydrocarbon groups of R¹⁴ and the divalent hydrocarbon groups of R¹⁵ are as delineated above. It is preferred that both D' and R¹⁴ are methyl radicals and that R¹⁵ is ethylene or trimethylene.

25 The urethane group of R¹⁵ is exemplified by a group having the formula -R¹⁶CO(NH₂)OC₂H₅- wherein R¹⁶ is a divalent hydrocarbon radical as described above.

30 The amount of silicone glycol copolymer employed varies depending on the amounts of components (A), (B) and (C) that are employed. It is preferred that from 0.50 to 50 weight parts of silicone glycol copolymer be used, and it is highly preferred that from 1 to 10 weight parts be employed, said weight parts being based on 100 weight parts of the reaction product of (I).

35 The reaction mixture of (I) can further comprise water. The amount of water to be added is not critical and is readily determined by routine experimentation. It is preferred that water comprise less than 1 weight part, said weight parts being based on the total weight of the reaction product.

40 The method of making the aerosol suppressant compositions of this invention can further comprise heating the reaction mixture of (I) and any optional compounds. Heating of the mixture of (I) is optional, however, if heat is applied it is preferred that the mixture of (I), including any optional components, is heated at a temperature range of 20°C. to 200°C. and it is more highly preferred that the mixture be heated at a temperature range of 100 to 150°C.

45 Compounds (A), (B), (C), and any optional components, can be mixed together using any suitable mixing means, such as a spatula; a drum roller; a mechanical stirrer, a three roll mill, a sigma-blade mixer, a bread dough mixer and a two roll mill. Compounds (A) and (B) and catalyst (C) can be prepared by homogeneously mixing (A), (B), (C), and any optional compounds, in any order. The order of mixing (A) to (C) and any optional components is not critical; however, it is preferred that catalyst (C) be brought together in the presence of compounds (A) and (B). It is highly preferred to mix compounds (A), (B), and any optional compounds, in a preliminary mixing step followed by addition of catalyst (C).

50 Mixing of compounds (A), (B), any optional compounds and catalyst (C) results in the formation of a reaction product.

The present invention further provides a method of making a curable silicone coating composition comprising adding to a curable silicone coating composition an aerosol suppressant composition prepared according to the method described hereinabove.

55 The organosilicon compounds (i), (ii), and (iii) of compound (A) and catalyst (C) are as delineated above in our method of preparing the aerosol suppressant compositions of this invention, including preferred embodiments and preferred amounts thereof.

Compound (B) is also as delineated above for the aerosol suppressant compositions of this invention, including preferred embodiments and amounts thereof. However, in our method of making the curable coating compositions of this invention, R in compound (B) can be the same or different as desired. It is preferred, however, that the group R is the same on both molecular chain ends of Compound (B).

60 Compounds suitable as (B) in this aspect of the invention include compounds having their formula selected from the group consisting of H₂C=CH-(CH₂)_b-O-(C₂H₄O)_x-(C₃H₆O)_y-(CH₂)_b-CH=CH₂, CH₃-CH=CH-(CH₂)_b-O-(C₂H₄O)_x-(C₃H₆O)_y-(CH₂)_b-CH=CH-CH₃, HO-(C₂H₄O)_x-(C₃H₆O)_y-H, H₂C=CH-(CH₂)_b-O-(C₂H₄O)_x-(C₃H₆O)_y-H and CH₃-CH=CH-(CH₂)_b-O-(C₂H₄O)_x-(C₃H₆O)_y-H, wherein b', x and y are as delineated hereinabove.

The curable silicone coating compositions can be any of the known curable silicone coating compositions known in the art. Thus, the curable silicone coating composition can comprise the well known System D coating compositions such as those disclosed in US-As 5,281,656, 5,036,117, 4,609,574, 4,774,111, 4,562,096, 4,256,870, 3,445,420, 4,476,166, 4,980,440, 4,736,048, 4,954,554, 5,095,067, 5,104,927, 4,961,963, 4,559,396, 4,465,818 and 4,472,563 which teach curable silicone coatings that are suitable. This list is not intended as a restriction on the type of curable silicone coatings to which our aerosol suppressant compositions can be added but it is disclosed to exemplify those coating compositions suitable for use in this method.

Thus, suitable curable silicone coating compositions include compositions which comprise (i) an organosilicon compound having at least two groups selected from olefinic hydrocarbon radicals having from 2 to 14 carbon atoms or hydroxyl groups, (ii) an organohydrogensilicon crosslinking agent, (iii) a metal catalyst and (iv) an inhibitor.

The olefinic hydrocarbon radicals or hydroxyl groups are as delineated above in our method of preparing the aerosol suppressant compositions of this invention, including preferred embodiments thereof. Preferred olefinic hydrocarbon containing polydiorganosiloxanes for use as organosilicon compound (i) also include the olefinic functional organopolysiloxanes delineated above, including preferred embodiments thereof. It is especially preferred that polydiorganosiloxanes contain either vinyl functional groups or 5-hexenyl functional groups.

It is preferred that from greater than zero to 95 weight parts of (i) be used, and it is highly preferred that from 90 to 99 weight parts of (i) be employed, said weight parts being based on the total weight of the curable silicone coating composition.

The organohydrogenpolysiloxanes for component (ii) are also as delineated above in our method of making the aerosol suppressant compositions, including preferred embodiments thereof.

It is preferred that from 1 to 20 weight parts of component (ii) be used, and it is highly preferred that from 1 to 5 weight parts of component (ii) be employed, said weight parts being based on the total weight of the curable silicone coating composition.

Component (iii) can be any platinum group metal-containing catalyst component. By platinum group, it is meant herein ruthenium, rhodium, palladium, osmium, iridium, platinum and complexes thereof. The platinum group catalysts suitable for our curable silicone coating compositions are the same as the platinum catalysts delineated above in our method of making the aerosol suppressant compositions, including preferred embodiments thereof. Preferred platinum-containing catalysts include chloroplatinic acid, either in hexahydrate form or anhydrous form, and chloroplatinic acid which is reacted with an aliphatically unsaturated organosilicon compound such as divinyltetramethylsiloxane. Preferably, component (iii) is present in an amount at 0.01 to 1 weight parts, and it is highly preferred to use from 0.1 to 0.5 weight parts, said weight parts being based on the total weight of the curable silicone coating composition.

The inhibitor (iv) can be any material that is known to be, or can be, used to inhibit the catalytic activity of platinum group metal-containing catalysts. The term "inhibitor" herein means a material that retards the room temperature curing of a curable mixture of Components (i), (ii) and (iii), when incorporated therein in small amounts, such as less than 10 parts by weight of the composition, without preventing the elevated curing of the mixture. Examples of suitable inhibitors include ethylenically or aromatically unsaturated amides, acetylenic compounds, ethylenically unsaturated isocyanates, olefinic siloxanes, unsaturated hydrocarbon diesters, conjugated ene-ynes, hydroperoxides, nitriles and diaziridines.

Preferred inhibitors include the acetylenic alcohols disclosed in US-A 3,445,420, including ethynylcyclohexanol and methylbutynol; the unsaturated carboxylic esters such as diallyl maleate and dimethyl maleate; maleates and fumarates such as those claimed in US-As 4,562,096 and 4,774,111, including diethyl fumarate, diallyl fumarate and bis-(methoxyisopropyl) maleate, and conjugated ene-ynes such as those described in US-As 4,465,818, 4,472,563 and 4,559,396. The above-mentioned patents teach how to prepare compounds which are suitable for use as an inhibitor in the compositions of this invention. Maleates and fumarates are the preferred inhibitors for this invention. More particularly, bis-methoxyisopropyl maleate and diethyl fumarate are preferred as inhibitors for our invention. It is preferred that from 0.02 to 10 weight parts of inhibitor be added to the total curable silicone coating composition and it is highly preferred that from 0.02 to 1 weight part be used, said weight parts being based on the total weight of the curable silicone coating composition.

Our curable coating compositions can additionally comprise (v) a bath life extender compound in a total amount sufficient to further retard the curing reaction at room temperature such as those described in US-A 5,036,117. Examples of suitable bath life extender compounds include compounds which contain one or more primary or secondary alcohol groups, carboxylic acids (including compounds which yield carboxylic acids when exposed to water at room temperature), cyclic ethers and water. Included in this group are the primary and secondary alcohols; diols and triols, such as ethylene glycol, propylene glycol and glycerine; partial ethers of diols and triols, such as 2-methoxyethanol, 2-methoxypropanol and 2-methoxyisopropanol; tetrahydrofuran; water and aqueous solutions of mineral acids, alkalis and salts. Primary and secondary alcohols, preferably having fewer than 10 carbon atoms are the most preferred for our invention. Examples thereof include methanol, 1-butanol, 2-butanol, tetradecanol and other alkanols such as ethanol, and normal- and isopropanol, iso-butanol, and the normal-, secondary- and iso-pentanols, -hexanols, -heptanols and -octanols; benzyl alcohol, phenol, and other aromatic alcohols such as methylphenyl carbinol, and 2-phenylethyl alcohol; allyl alcohol and cyclohexanol. It is highly preferred that the bath life extender is benzyl alcohol or water.

The amount of bath life extender (v) that is used can be as high as 10 parts or more by weight. Preferably, the amount of bath life extender falls within the range of 0.01 to 5 parts, and most preferably 0.01 to 1 part by weight, based on the total weight of the curable silicone coating composition.

These curable silicone coating compositions can further comprise a solvent. Examples of solvents include aliphatic

5 hydrocarbons such as pentane, hexane, heptane, octane and nonane; aromatic hydrocarbons such as benzene, toluene and xylene; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone, and halogenated diluents such as fluorine-, chlorine- and bromine-, substituted aliphatic or aromatic hydrocarbons such as trichloroethane, perchloroethylene and bromobenzene. Two or more of these solvents may also be used together.

10 The amount of solvent is not critical and may be readily determined by one skilled in the art. Our curable silicone coating compositions may contain up to 99 weight parts of solvent; however, it is preferred that the solvent, if employed, ranges from 70 to 90 weight parts of the composition, said weight being based on the total weight of the curable silicone coating composition.

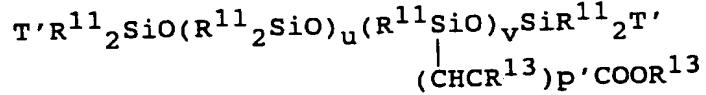
15 The curable silicone coating compositions can further comprise any of the well known high release additives in the art. This additive is preferably a vinyl-functional MQ resin (silicone resins consisting of monovalent (M) units ($R^{17}3SiO_{1/2}$) wherein R^{17} is selected from the group consisting of olefinic hydrocarbon groups as delineated hereinabove, monovalent hydrocarbon groups free of aliphatic unsaturation as delineated above or a mixture of these groups) and quadrivalent (Q) (SiO_2 units) diluted with a linear olefinic containing siloxane polymer such as those delineated above (i.e. vinyl- or hexenyl-functional polydiorganosiloxanes). The high release additive preferably comprises 40 to 70 weight parts of the vinyl-functional MQ resin and 30 to 60 weight parts of the olefinic containing siloxane polymer. From 1 to 99 weight parts 20 of the high release additive may be employed in our curable coatings, and preferably 1 to 10 weight parts of high release additive is employed, said weight being based on the total weight of the curable silicone coating.

25 Our curable silicone coating compositions can also contain any optional components commonly used in platinum-group metal catalyzed organosilicon compositions, such as reinforcing and extending fillers, hydrocarbons and halohydrocarbons free of aliphatic unsaturation, colorants, stabilizers, adhesion modifiers and adhesive-release modifiers.

30 The curable silicone coating of our invention can also be any of the radiation curable silicone coating compositions known in the art, such as UV (ultraviolet) or EB (electron beam) curable silicone coatings. Thus, our curable silicone coating composition can comprise any of the well known radiation curable silicone coating compositions of the art, such as those disclosed in US-As 4,617,238; 5,057,549; 5,145,915; 5,270,423 and 5,331,020; EP-A 0462389, CA Application No. 2,035,369 or PCT Patent Application No. 9322369, which teach suitable radiation curable silicone coatings. This list is not intended as a restriction on the type of radiation curable coatings to which the aerosol suppressant compositions of this invention can be added, but is disclosed merely to exemplify suitable radiation curable silicone coatings.

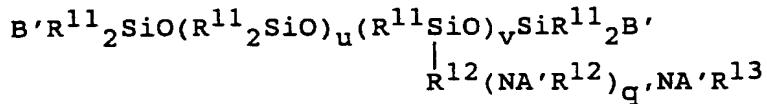
35 Thus, our curable silicone coating composition can also comprise (i) a radiation curable organosilicon compound having at least two groups selected from the group consisting of epoxy groups, vinyl ether groups, acrylamide groups, acrylate groups, and olefinic hydrocarbon radicals having from 2 to 14 carbon atoms and (ii) an initiator. Preferably, the organosilicon compound (i) is selected from the group consisting of vinyl ether-containing polyorganosiloxanes, epoxy-containing organopolysiloxanes, acrylate-containing organopolysiloxanes, acrylamide-containing organopolysiloxanes, vinyl-containing organopolysiloxanes and hexenyl-containing organopolysiloxanes. The vinyl ether-containing polyorganosiloxanes, epoxy-containing organopolysiloxanes and olefinic hydrocarbon containing organopolysiloxanes are as delineated above in our method of making the aerosol suppressant compositions of this invention, including preferred 40 embodiments thereof.

Preferred acrylate functional organopolysiloxanes have the general formula



50 wherein R^{11} and R^{13} are as defined above, T' denotes R^{11} or $-(CHCR^{13})_p COOR^{13}$, u and v are as defined above, p has a value of 1 to 10, with the proviso that there are at least two $-(CHCR^{13})_p COOR^{13}$ groups per compound. Preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

55 Acrylamide functional organopolysiloxanes suitable as organosilicon compound (i) have been disclosed in US-As 4,608,270, 4,831,064, 4,911,986, 5,017,717, 5,082,958 and 5,087,716 which disclose acrylamide functional organopolysiloxanes that can be used as radiation curable organosilicon compound (i) in these curable coating compositions. Preferred acrylamide-containing organopolysiloxanes have the general formula



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10 wherein R¹¹, R¹² and R¹³ are as defined above, q' has a value of 0 or 1, B' denotes R¹¹ or -R¹²(NA'R¹²)_q, NA'R¹³, u and v are as defined above, A' denotes an acyl radical selected from -C(O)CH=CH₂ or -C(O)C(CH₃)=CH₂, with the proviso that there are at least two -R¹²(NA'R¹²)_q, NA'R¹³ groups per compound. Preparation of such compounds is well known in the organosilicon art and needs no extensive delineation herein.

15 It is preferred that from 95 to 99.5 weight percent of the radiation curable organosilicon compound (i) be used in our radiation curable coating compositions and it is highly preferred that from 97 to 99 weight percent of this compound be employed, said weight percent being based on the total weight of the radiation curable silicone coating composition.

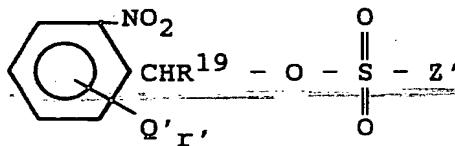
20 Compounds suitable as the initiator (ii) include photoinitiators and sensitizers. Sensitizers have been described in great detail in the art in numerous publications and include materials such as the well known material benzophenone. Suitable initiators include onium salts, certain nitrobenzyl sulfonate esters, diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids.

25 Suitable onium salts as (ii) in the radiation curable silicone coatings of this invention have the formulae R¹⁸₂IM'X_n⁻, R¹⁸₃S⁺M'X_n⁻, R¹⁸₃Se⁺M'X_n⁻, R¹⁸₄P⁺M'X_n⁻ and R¹⁸₄N⁺M'X_n⁻, wherein R¹⁸ is the same or different organic radicals having from 1 to 30 carbon atoms. These include aromatic carbocyclic radicals of from 6 to 20 carbon atoms, which can be substituted with from 1 to 4 monovalent hydrocarbon radicals selected from alkoxy radicals having from 1 to 8 carbon atoms; alkyl radicals having from 1 to 8 carbon atoms; nitro, chloro, bromo, cyano, carboxyl, mercapto and aromatic heterocyclic radicals including pyridyl, thiophenyl and pyranyl. The symbol M' denotes metals or metalloids which include transition metals such as such as Sb, Fe, Sn, Bi, Al, Ga, In, Ti, Zr, Sc, V, Cr, Mn and Cs; rare earth metals such as the lanthanides, for example, Cd, Pr and Nd and metalloids such as B, P or As. M'X_n⁻ is a non-basic, non-nucleophilic anion, such as BF₄⁻, PF₆⁻, AsF₆⁻, SbF₆⁻, SbCl₆⁻, HSO₄⁻, ClO₄⁻, FeCl₄⁻, SnCl₆⁻, BiCl₅⁻ and the like.

30 Bis-diaryl iodonium salts, such as bis(dodecyl phenyl) iodonium hexafluoroarsenate and bis(dodecylphenyl) iodonium hexafluoroantimonate and dialkylphenyl iodonium hexafluoroantimonate are preferred. Nitrobenzyl sulfonate esters which are useful as photoinitiators in the compositions of the present invention have the general formula

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45 wherein Z' is selected from the group consisting of alkyl groups, aryl groups, alkylaryl groups, halogen substituted alkyl groups, halogen substituted aryl groups, halogen substituted alkylaryl groups, nitro substituted aryl groups, nitro substituted alkylaryl groups, aryl groups having nitro and halogen substituents, alkylaryl groups having nitro and halogen substituents, and a group having the formula -C₆H₄SO₃CHR¹⁹C₆H_{4-r}Q'_r(NO)₂. R¹⁹ is selected from the group consisting of hydrogen atom, methyl and nitro-substituted aryl groups. Each Q' is independently selected from the group consisting of hydrocarbon groups, hydrocarbonoxy groups, NO₂, halogen atoms and organosilicon compounds. r' has a value of 0, 1 or 2, with the proviso that Q' is not an acidic group. These nitrobenzyl sulfonate photoinitiators are more fully described in EP Application 92310164.6 published as EP-A 0542485.

50 Diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids are also suitable as initiator (ii) in our radiation curable silicone coatings. Preferred diaryliodonium salts of sulfonic acid are selected from diaryliodonium salts of perfluoroalkylsulfonic acids and diaryliodonium salts of aryl sulfonic acids. Preferred diaryliodonium salts of perfluoroalkylsulfonic acids include diaryliodonium salts of perfluorobutanesulfonic acid, diaryliodonium salts of perfluoroethanesulfonic acid, diaryliodonium salts of perfluoro-octanesulfonic acid and diaryliodonium salts of trifluoromethane sulfonic acid. Preferred diaryliodonium salts of aryl sulfonic acids include diaryliodonium salts of para-toluene sulfonic acid, diaryliodonium salts of dodecylbenzene sulfonic acid, diaryliodonium salts of benzene sulfonic acid and diaryliodonium salts of 3-nitrobenzene sulfonic acid.

Preferred triarylsulfonium salts of sulfonic acid are selected from triarylsulfonium salts of perfluoroalkylsulfonic acids or triarylsulfonium salts of aryl sulfonic acids. Preferred triarylsulfonium salts of perfluoroalkylsulfonic acids include triarylsulfonium salts of perfluorobutanesulfonic acid, triarylsulfonium salts of perfluoroethanesulfonic acid, triarylsulfonium salts of perfluoro-octanesulfonic acid and triarylsulfonium salts of trifluoromethane sulfonic acid. Preferred triarylsulfonium salts of aryl sulfonic acids include triarylsulfonium salts of para-toluene sulfonic acid, triarylsulfonium salts of dodecylbenzene sulfonic acid, triarylsulfonium salts of benzene sulfonic acid and triarylsulfonium salts of 3-nitrobenzene sulfonic acid.

Preferred diaryliodonium salts of boronic acids, and triarylsulfonium salts of boronic acids are compounds such as those disclosed in EP-A 0562922. Preferred diaryliodonium salts of boronic acids include diaryliodonium salts of perhaloarylboronic acids and preferred triarylsulfonium salts of boronic acids are the triarylsulfonium salts of perhaloarylboronic acid.

The initiators (ii) may be present in any proportion which effect curing in the compositions of this invention. Preferably, the amount of initiator is from 0.1 to 10 weight percent based on the total weight of the composition, and it is highly preferred to use between 1 and 5 weight percent based on the total weight of our radiation curable silicone coating composition.

These radiation curable silicone coatings can further contain optional ingredients such as photosensitizers, fillers, high release additives, reactive diluents such as organic vinyl ethers, photochromic materials, dyes, colorants, preservatives, fragrances and other radiation curable compounds may be included in the composition. Preferably, no more than 25 parts by weight of the composition is constituted by these optional ingredients.

Our aerosol suppressant composition is added to our curable silicone coating composition in amount sufficient to reduce the mist (aerosol) of the coating during high speed processes. This amount can readily be determined by one skilled in the art through routine experimentation. It is preferably added to the curable silicone coating composition in an amount of 0.5 to 50 weight parts and it is highly preferred that the aerosol suppressant composition is added in an amount of 1 to 3 weight parts, said weight parts being based on 100 weight parts of the curable silicone coating composition.

The method of making the curable silicone coating compositions of this invention can further comprise neutralizing the reaction product after (I). Methods of neutralizing the reaction product of step (I) are as delineated above in the method of making our aerosol suppressant compositions, including preferred embodiments thereof.

Our method of making the curable silicone coating compositions of the invention can further comprise filtering the reaction product of (I). These methods are also as delineated above in the method of making our aerosol suppressant compositions, including preferred embodiments thereof.

The reaction mixture of (I) can further comprise a monohydric alcohol having from 1 to 30 carbon atoms as delineated hereinabove in our method of making aerosol suppressant compositions, including preferred embodiments and preferred amounts thereof.

The method of making our curable silicone coating compositions can further comprise the step of adding a silicone glycol copolymer after (I). The silicone glycol copolymer is preferably added to the reaction product of (I) (i.e. after the reaction has gone to completion). The silicone glycol copolymer is as delineated hereinabove for the aerosol suppressant compositions of this invention, including preferred embodiments and preferred amounts thereof.

The reaction mixture of (I) can further comprise water. It is preferred that water comprise less than 0.1 weight part of the total reaction product.

The method of making the curable silicone coating compositions of this invention can further comprise heating the reaction mixture of (I). Heating of the reaction mixture of (I) is optional; however, if heat is applied, it is preferred that the mixture be heated at a temperature range of 20°C. to 200°C., and more highly preferred that the mixture be heated at a temperature range of 100 to 150°C.

When component (A) is organohydrogensilicon compound (i), the reaction mixture of (I) can further comprise an organic compound having at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy groups, amine groups, isocyanate groups, oxime groups, acetoxyl groups and mixtures thereof to the mixture of (I). The organic compounds are as delineated hereinabove for the aerosol suppressant compositions of this invention including amounts and preferred embodiments thereof.

The reaction mixture of (I) can further comprise a foam control agent. Preferably, the foam control agent is a fluorosilicone polymer. The fluorosilicone polymers are as delineated hereinabove for our aerosol suppressant compositions, including amounts and preferred embodiments thereof.

The present invention further relates to a method of suppressing mist in a curable silicone coating composition, comprising adding a liquid having a surface tension of greater than or equal to 25 dynes/centimeter to our curable silicone coating composition. It has been found through extensive experimentation that liquids having a surface tension of at least 25 dynes/centimeter act to suppress mist in silicone coatings. Liquids meeting this criteria, and thus capable of reducing mist in silicone coatings, include benzyl alcohol, polyethylene glycol, ethylene glycol, glycerol, 1,2-propanediol and water. The amount of liquid in our curable silicone coating preferably ranges from 5 to 20 weight parts per 100 weight

parts of curable silicone coating. It is highly preferred that the liquid comprises from 5 to 10 weight per 100 weight parts of curable silicone coating.

The present invention also relates to a method of improving the anchorage of a curable silicone coating composition to a substrate comprising adding the aerosol suppressant composition of our invention to our curable coating composition of the invention, and then applying and curing said curable coating composition on said substrate.

The present invention further relates to a method of making a cured coating, the method comprising the steps of: (I) adding an aerosol suppressant composition to a curable silicone coating composition; (II) coating the mixture from (I) on the surface of a substrate; (III) exposing the coating and the substrate to atmospheric moisture or an energy source selected from (i) heat or (ii) actinic radiation in an amount sufficient to cure the coating, wherein the aerosol suppressant composition is prepared according to our method described hereinabove. Compound (B) is as delineated above in the method of making the curable coating compositions of this invention, including preferred embodiments thereof (i.e. the R group can be the same or different as desired but is preferably identical on the molecular chain ends of compound (B)). This method can further comprise applying a pressure sensitive adhesive on the coating after step (III).

(B)). This method can further comprise applying a pressure sensitive adhesive on the sheet material. Actinic radiation means ultraviolet light; electron beam radiation; and alpha-, beta-, gamma- or x-rays. Heat means infrared radiation, hot-air and microwave radiation. Of course, actinic radiation is frequently accompanied by heat and the use of a combination of the two is possible in the present process. In the preferred process, the coating process is accomplished by any suitable manner known in the art, such as by spreading, brushing, extruding, spraying, gravure, kiss-roll and air-knife.

In a preferred embodiment, the solid substrate is a flexible sheet material such as paper, polyolefin film and polyolefin-coated paper or foil. Other suitable solid substrates coated by this invention include other cellulosic materials such as wood, cardboard and cotton; metallic materials such as aluminum, copper, steel and silver; siliceous materials such as glass and stone; and synthetic polymer materials such as polyolefins, polyamides, polyesters and polyacrylates. As to form, the solid substrate can be substantially sheet-like, such as a peelable release liner for pressure sensitive adhesive; a fabric or a foil; or substantially three-dimensional in form.

25 After our liquid curable composition has been coated onto a substrate, it is heated and/or irradiated with actinic radiation to cure the liquid coating and to adhere it to the substrate.

In a preferred embodiment of our process, a flexible sheet material, such as paper, metal foil or tapestock, is coated with a thin coating of the liquid curable composition, preferably in a continuous manner. Then, the thus-coated material is heated and/or irradiated to rapidly cure the coating, to provide a sheetlike material bearing on at least one surface thereof an adhesive-releasing coating. The adhesive-releasing coating is subsequently brought into contact with a pressure sensitive adhesive, preferably in an in-line manner, to form an article having a peelable, i.e. releasable, adhesive/coating interface. Examples of such an article include, adhesive labels having a peelable backing, adhesive tape in roll form and adhesive packaged in a strippable container. The pressure sensitive adhesive can be non-silicone-based, such as the well-known acrylic or rubber types or it can be silicone-based, such as the peroxide- or platinum-curable polydilorganosiloxane-based adhesives.

The process of this invention is also applicable to adhesive materials, other than pressure sensitive adhesives. Examples of said adhesive materials include foods, graphite composites, asphalt and gum polymers.

The following examples are presented to further teach the invention. All amounts (parts and percentages) are by weight unless otherwise indicated.

To analyze and quantify the silicone mist in a reproducible manner, a laboratory 2-roll coater capable of running 100-150 cm/min (2,000 ft/min) of line speed was built. Once we were able to generate the mist in a controlled manner,

To analyze and quantify the silicone mist in a reproducible manner, a laboratory 2-roll coater capable of running over 609.6 m/min (2,000 ft/min) of line speed was built. Once we were able to generate the mist in a controlled manner, a sophisticated particle size analyzer was attached to the machine to characterize the mist.

The 2-roll coater was equipped two 15.24 cm (6 inch) diameter rollers (bottom roll: rubber coated and top roll: chrome coated), two blades, one on each roll and a bottom pan for containing the liquid supply. The rubber coated bottom roll was driven by variable speed motor which can cover over 609.6 m/min (2,000 ft/min) of line speed. The top roll was a nipping roll which is engaged with bottom roll by applying pressure. Since the measurement of mist is very sensitive to the environment the whole system was located in a hood and the hood fan speed was kept low to minimize the influence of turbulence on the measurement. A vacuum cleaner was attached to each roll surface by using a coat hanger type accessory to sweep the mist away once it passed the measuring point. The coating liquid was supplied either from the button pan or a dam on the top blade against the top metal roller. The bottom pan feeding method was employed for all data reported herein. To obtain consistent results, the pressure settings of top blade and top roller were kept at 69.5 and 344.7 kPa (10 and 50 psi), respectively, and the bottom blade was used as a doctoring blade to regulate the amount of incoming fluid. The coater was made by Euclid Tool and Machines, Bay City, MI.

55 The air borne silicone particles produced by the "mist generator" described above were drawn to a QCM Cascade Impactor™, (Model PC-2 Ten Stage, California Measurements, Inc., Sierra Madre, CA) and analyzed. A complete analysis of aerosol mass concentration and size distribution was obtained from a sample of air taken for a short period of time (10 seconds to 1 minute). Collected samples of the sized particles were retained undisturbed (if the particles were solid) and were used directly to obtain composition, size and shape (for solid particles only) information using auxiliary scanning electron microscopy (SEM) and other analytical techniques.

The instrument separated aerosol particles into 10 sizes from 0.05 to 25 micrometers. It did this by drawing the aerosol-laden air sample through a series of 10 stages, each stage containing an inertial impactor jet of decreasing size (various size of orifices), where the particles are accelerated. Directly below each jet was a piezoelectric quartz crystal that was used as an impactor to collect the separated particles. As the jet of air exited from the nozzle, it was forced to turn sharply to flow around the crystal. Larger particles in the stream, because of their inertia, continued to travel toward the crystal plate and impact on it. Smaller particles followed the flow of air around the crystal to the next stage, which was a repeat of the proceeding stage, except it was equipped with a smaller nozzle that was designed to impact smaller particles. The 10 stages thus collected particles of smaller and smaller sizes. Each crystal was the frequency-controlling element of a quartz-crystal microbalance (QCM), whose output frequency decreased when particles were collected on the surface. Placed in close proximity to the sensing crystal, but shielded from the collected particles, was an identical reference crystal controlling the frequency of another circuit set about 2kHz higher than that of the sensing crystal. The set of crystals in a stage were closely matched in frequency.

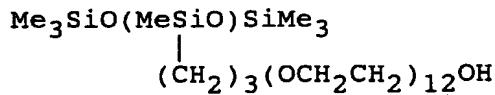
The beat frequency between the two oscillators was the signal indicative of the mass collected. The particle size distribution was obtained by monitoring the frequency change of the QCM in each of the 10 stages.

A tip of stainless steel tube 6.4 mm (1/4" diameter) remoted from the QCM Cascade Impactor™ was placed very closely to the nip point of the mist generator. To start the measurement, the impactor was initialized by pushing the initialization button on the front panel of the control unit. The mist generator was set at a speed (either 304.8, 457.2 or 609.6 m/min [1,000, 1,500 or 2,000 ft/min]) and allowed to run for 10 seconds before taking the sample and then opening the sampling knob of the impactor for a predetermined period of time (10 to 30 seconds). After sampling, the impactor was left to idle for an additional 50 seconds to let the particles settle in the stages. The amount of collected particles at each stage was calculated by pushing the "final" button on the front panel. The result of the total amount of mist and particle size distribution was printed out to both the CRT of the PC, connected via the serial port and to the thermal printer on the controller. The data was taken from at least the average of three individual runs at a speed. When the individual data scattered too much, two more measurements were made and then the two extreme values (1 highest and 1 lowest) were discarded before the results were averaged.

Tests were also conducted on a 30.5 cm (12") forward roll coater. On a five 30.5 cm (12 inch) diameter production scale, forward roll-coater, the QCM Cascade Impactor™ was installed to measure the amount of mist produced at 457.2 m/min (1,500 ft/min) line speed. The tip of stainless steel tube 6.4 mm (1/4" diameter) for sample collection was located at 2.5 cm (1 inch) away from the nip point of the applicator and nipping rollers of the coater. The coater was run for 10 seconds at 457.2 m/min (1,500 ft/min) and then the mist sample was taken for an additional 10 seconds. Two to three data points were taken at a condition and then the average was taken as a result. The average variations were less than 15% of the mean values. In the examples, Me denotes methyl, Hex denotes hexenyl and Ac denotes acetyl.

Examples 1-12

The aerosol suppressant effect of the compositions of the instant invention were tested. Into a 500 ml 3-neck flask were added 100 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 12 and 50 mole percent of methylhydrogen moiety on the siloxane chain, .01 part of a dimethylvinylsiloxy-endblocked polydimethylsiloxane-polymethylperfluorobutylethylsiloxane-methylvinylsiloxane copolymer, having a degree of polymerization of 300 and 10 parts (15 parts in Example 10) of polypropylene glycol having an average molecular weight of 2000. In examples 5-12, an amount of oleyl alcohol or stearyl alcohol was also added to this mixture, the type and amount (parts per 100 parts of methylhydrogensiloxane copolymer) of alcohol are given in Table I. Next, the mixture was heated to a temperature of from 120 to 130°C. and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. The reaction temperature was then cooled to room temperature. Next, in Examples 1-4, .05 part of a 1 percent by weight solution of potassium silanolate in toluene was added to this mixture with stirring and this mixture was then purged with nitrogen gas in the flask. In Examples 5-12, however, .05 part of a 10 percent by weight solution of potassium silanolate in xylene was added to the mixture with stirring and the mixture was then purged with nitrogen gas in the flask. Additional catalyst was then added to the mixture at room temperature to increase the viscosity of the reaction product until a target viscosity was obtained. When the viscosity of the reaction product reached the target viscosity, small pieces of dry ice were added to the flask to neutralize the basic catalyst. The neutralized salt was then removed through a pressure filter. In Examples 3 and 4, 5 parts of a silicone glycol copolymer having the average formula:



5 10 were added to 100 parts of the above reaction product.

15 Next, 2 parts of the above prepared reaction product were added to 100 parts of two types of Curable Coatings, A and B, which are delineated hereinbelow. Curable Coating A comprised 100 parts of an organopolysiloxane having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{Me}_2\text{SiO})_b\text{SiMe}_3\text{Hex}$ wherein said organopolysiloxane had 2 mole percent of hexenyl groups and an average degree of polymerization of 150. Curable Coating B comprised a mixture of 97.4 parts of Curable Coating A, 1.8 parts of a platinum catalyst (a soluble platinum complex containing 0.67% platinum formed from chloroplatinic acid and divinyltetramethyldisiloxane), 0.8 part of bis(2-methoxy-1-methylethyl) maleate, and 4.1 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 40 and 70 mole percent methylhydrogen moiety on the siloxane chain. The curable silicone coatings containing the reaction product of the instant invention were then tested for the amount of silicone mist generated off a coater as described above. The results of this test are listed in Table I. In all of the examples in Table I, except for Example 1, high shear was applied for 5 minutes to the curable coatings by using a Turrax™ Mixer prior to the coating being tested for mist. In Examples 1 and 2, only the reaction product of the instant invention was added to the curable coating, no alcohol or silicone glycol copolymer was employed during the formation of the reaction product in these two examples. As a comparison, the amount of mist generated by Curable Coatings A and B, without the reaction product of this invention, was also measured and this is also given in Table I as the Comparison (Comp.) Coating.

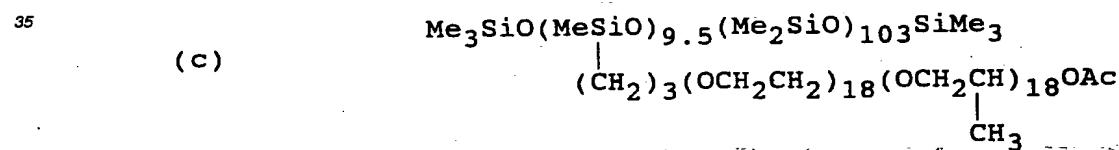
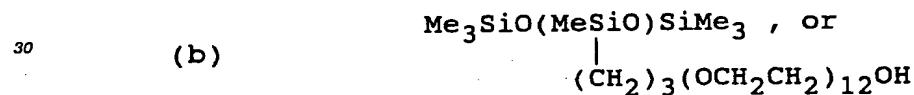
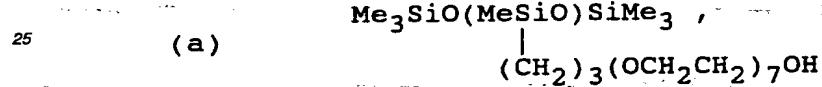
Table I

30	Curable Coating Ex.	Total Mist (mg/m ³)					
		Additiv		457.2 m/min.		609.6 m/min.	
35	Type	Amount (parts)	Invention	Comp. Coating	Invention	Comp. Coating	
40	1 A	0	0.05	3.69	0.12	8.19	
45	2 A	0	0.56	2.51	2.15	10.56	
50	3 A	Si Glycol Copolymer	5	0.08	2.09	0.24	8.37
55	4 B	Si Glycol Copolymer	5	2.59	4.13	19.75	22.39
	5 B	Oleyl	5	0.23	3.17	0.87	5.47
	6 B	Oleyl	10	0.16	3.17	0.32	5.47
	7 B	Oleyl	10	0.16	1.58	0.79	4.78
	8 B	Oleyl	15	0.08	1.58	0.28	4.78
	9 B	Oleyl	20	0.34	1.58	1.63	4.78
	1 B	Oleyl	10	1.32	1.68	2.44	5.13
	1 B	n-stearyl	10	1.68	1.68	4.33	5.13
	1 B	i-stearyl	5	0.76	1.35	2.93	5.58

55 As seen from Table I, curable coating compositions containing the reaction product of the instant invention, with or without an additive, had significant reductions in the amount of mist coming off the coater during high speeds, in comparison to curable coatings which did not contain the reaction product of this invention.

Examples 13-28

5 A reaction product was prepared according to the procedure described in Examples 1-12. However, in this instance, one of three different silicone glycol copolymers in varying amounts were added to the reaction product prior to addition of the catalyst. This reaction product was then tested for its effect on the amount of misting coming off of the coater. Into a 500 ml 3-neck flask were added 100 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 12 and 50 mole percent of methylhydrogen moiety on the siloxane chain, .01 part of a dimethylvinylsiloxy-endblocked polydimethylsiloxane-polymethylperfluorobutylethylsiloxane-methylvinylsiloxane copolymer having a degree of polymerization of 300, and 10 parts of polypropylene glycol 10 having an average molecular weight of 2000. Next, the mixture was heated to a temperature of from 120 to 130°C. and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. The reaction temperature was then cooled to room temperature. Next, .05 part of 1 percent by weight solution of potassium silanolate in toluene was added to this mixture with stirring and this mixture was then purged with nitrogen gas in the flask. Additional catalyst was then added to the mixture at room temperature to increase the viscosity 15 of the reaction product until a target viscosity was obtained. When the reaction product reached the target viscosity, small pieces of dry ice were added to the flask to neutralize the basic catalyst. The neutralized salt was then removed through a pressure filter and the solvent was stripped using a rotoevaporator. Then, 2 parts of each of the above prepared reaction products were separately added to 100 parts of a curable coating comprising 100 parts of an organopolysiloxane having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeHexSiO})_b\text{SiMe}_2\text{Hex}$ wherein said organopolysiloxane had 2 mole 20 percent of hexenyl groups and an average degree of polymerization of 150. Next, one of the three different types of silicone glycol copolymer delineated below were added to this mixture, the copolymers having the average formulae:



40 were added to 100 parts of the above reaction product. The type and amount of each silicone glycol copolymer added is listed in Table II. The three curable coatings, each containing one of the above prepared reaction products of the instant invention, were then tested for the amount of silicone mist generated from the coater, as described above. The results are also reported in Table II. In all the examples, except Examples 13 and 14, high shear was applied for 5 minutes to the curable coatings containing the reaction product of the instant invention by using a Turrax™ Mixer prior to the coating being tested for mist. In Examples 13, 14, 21 and 25, the reaction product of the instant invention was entirely 45 omitted from the curable coating (i.e. the curable coating itself was tested). In Example 15, only the reaction product of the instant invention was added to the curable coating; no alcohol or silicone glycol copolymer was employed during the formation of the reaction product in this example.

Table II

Example	Si Glycol Copolymer		Total Mist (mg/m ³)	
	Type	Amount (parts)	457.2 m/min.	609.6 m/min.
13	-	0	2.51	10.57
14	-	0	2.30	9.47
15	-	0	0.09	0.14
16	-	0	0.56	2.15
17	a	5	0.11	0.45
18	a	10	0.09	0.30
19	a	20	0.07	0.45
20	a	40	0.18	0.65
21	b	0	2.09	8.37
22	b	5	0.08	0.24
23	b	10	0.11	0.46
24	b	20	0.18	0.49
25	c	0	2.09	8.37
26	c	5	0.12	0.49
27	c	10	0.11	0.35
28	c	20	0.16	0.75

As seen from Table II, curable coating compositions containing the reaction product of the instant invention, with or without an additive, had significantly lower misting values, in contrast to the curable coatings which did not contain the reaction product of this invention.

Examples 29-34

Then, the effect of adding a monohydric alcohol to the reaction product of the instant invention was tested. Into a 500 ml 3-neck flask were added 100 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 12 and 50 mole percent of methylhydrogen moiety on the siloxane chain, .01 part of a dimethylvinylsiloxy-endblocked polydimethylsiloxane-polymethylperfluorobutylethylsiloxane-methylvinylsiloxane copolymer having a degree of polymerization of 300, and 10 parts of polypropylene glycol having an average molecular weight of 2000. Next, 15 parts of oleyl alcohol were added to 100 parts of this mixture. The mixture was then heated to a temperature of from 120 to 130°C. and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. The reaction temperature was then cooled to room temperature. Thereafter, .05 part of a 10 percent by weight solution of potassium silanolate in xylene was added to the mixture with stirring and the mixture was then purged with nitrogen gas in the flask. Additional catalyst was then added to the mixture at room temperature to increase the viscosity of the reaction product until a target viscosity was obtained. When the reaction product reached the target viscosity, small pieces of dry ice were added to the flask to neutralize the basic catalyst. The neutralized salt was then removed through a pressure filter and the solvent was stripped using rotoevaporator.

An amount of the above prepared reaction product, listed in Table III, was then added to 100 parts of a curable coating comprising 97.4 parts of an organopolysiloxane having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeHexSiO})_b\text{SiMe}_2\text{Hex}$ wherein said organopolysiloxane had 2 mole percent of hexenyl groups and an average degree of polymerization of 150, 1.8 parts of a platinum catalyst (a soluble platinum complex containing 0.67% platinum formed from chloroplatinic acid and divinyltetramethyldisiloxane), 0.8 part of bis(2-methoxy-1-methylethyl) maleate, and 4.1 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 40 and 70 mole percent of methylhydrogen moiety on the siloxane chain. The curable coatings, con-

taining the reaction products of the instant invention, were then tested for the amount of silicone mist generated from the coater, as described. The results are also reported in Table III. High shear was applied for 1 minute to the curable coating by using a Turrax™ Mixer prior to the coating being tested for mist. As a comparison, the amount of mist generated by the curable coating without our reaction product was also measured.

5

Table III

Example	Reaction Product (parts per 100 parts of curable coating)	Total Mist (mg/m ³)	
		457.2 m/min.	609.6 m/min.
29	0	1.71	5.17
30	0.5	0.66	2.95
31	1	0.33	0.80
32	1.5	0.10	0.33
33	2	0.11	0.28
34	3	0.19	0.72

25 As seen from Table III, curable coating compositions containing the reaction product of the instant invention had significantly lower misting values, in contrast to curable coatings which did not contain the reaction product of this invention.

30 **Examples 35-45**

35 The anti-misting effect of various additives, having a variety of surface tensions was tested in curable silicone coatings. Thus, 10 parts of the various additives delineated in Table IV were added to 100 parts of a curable coating containing an organopolysiloxane having the general formula HexMe₂SiO(Me₂SiO)_a(MeHexSiO)_bSiMe₂Hex wherein said organopolysiloxane had 2 mole percent of hexenyl groups and an average degree of polymerization of 150. The resulting coating was then tested for its misting effect as delineated above. The surface tension of the particular additive is also listed in Table IV. Therein, PPG 2000™ denotes polypropylene glycol having a molecular weight of 2000 and PEG 600™ denotes polyethylene glycol having a molecular weight of 600.

40

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50

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Table IV

Example	Additive	Surface Tension at 20°C.	Total Mist (mg/m ³) 609.6 m/min.
35	-	-	7.46
36	Heptane	20.1	6.41
37	Toluene	27.93*	6.42
38	Xylene	28.5	5.52
39	PPG™ 2000	32.00	5.88
40	Benzyl Alcohol	35.5	1.51
41	PEG™ 600	43.00	1.84
42	Ethylene Glycol	48.4	0.09
43	Glycerol	62.9	1.41
44	1,2-propane diol	72*	1.73
45	Water	72.9	1.11

* at 25°C.

It is seen from Table IV that an organic liquid having a surface tension of greater than 32 dynes/centimeter has a significant effect on the amount of silicone mist generated by a curable silicone coating during high speed processing.

Examples 46-50

The aerosol suppressant effect of the compositions of the instant invention were further tested. Into a 1000 ml 3-neck flask were added 400 parts of a trimethylsiloxy-endblocked-methylhydrogensiloxane polymer having a an average degree of polymerization of 60 and 47 parts of polyethylene glycol having an average molecular weight of 600. Next, the mixture was heated to a temperature of 150°C. and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. Then, 3.72 parts of dry palladium on carbon (a 5% mixture) were added to this mixture with stirring. This mixture was heated at a temperature of 150°C. for 4 days. During this time, the mixture was also purged with nitrogen gas in the flask. The reaction temperature was then cooled to room temperature. The supported catalyst was then filtered.

An amount (delineated in Table V) of the above reaction product was then added to 100 parts of the silicone curable coating delineated below. The curable coating comprised 97.4 parts of an organopolysiloxane having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeHexSiO})_b\text{SiMe}_2\text{Hex}$ wherein said organopolysiloxane has 2 mole percent of hexenyl groups and an average total viscosity of 450 mm²/s, 1.8 parts of a platinum catalyst (a soluble platinum complex containing 0.67% platinum, formed from chloroplatinic acid and divinyltetramethyldisiloxane), 0.8 part of bis(2-methoxy-1-methyl-ethyl) maleate, and 4 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 40 and 70 mole percent of methylhydrogen moiety on the siloxane chain. The curable coating containing the reaction product of this invention was then tested for the amount of silicone mist generated from a 30.5 cm (12") forward roll coater according to the procedure above. The mean values of total mist are delineated in Table V.

Table V

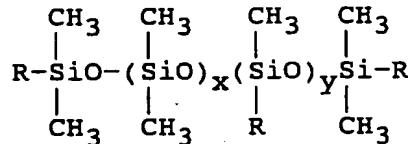
Example	Reaction Product (parts per 100 parts of curable coating)	Total Mist (mg/m ³)
		457.2 m/min.
46	0	3.54
47	1	0.56
48	2	0.42
49	3	0.26
50	4	0.26

As seen from Table V, curable coating compositions containing the reaction product of the instant invention had significantly lower misting values, in contrast to the curable coatings which did not contain our reaction product.

Examples 51-53

The aerosol suppressant effect of the compositions of our invention were next tested in radiation curable coating compositions. Into a 500 ml 3-neck flask were added 200 parts of a trimethylsiloxy-endblocked-polydimethyl-siloxane-methylhydrogensiloxane copolymer, having a total average degree of polymerization of 12 and 50 mole percent of methylhydrogen moiety on the siloxane chain, .03 part of a dimethylvinylsiloxy-endblocked-polydimethylsiloxane-polymethylperfluorobutylethylsiloxane-methylvinylsiloxane copolymer having a degree of polymerization of 300, 20 parts of polypropylene glycol having an average molecular weight of 2000, and 30 parts of oleyl alcohol. Next, the mixture was heated to a temperature of from 120 to 130°C., and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. The reaction temperature was then cooled to 90°C. Then, 0.1 part of a 5 percent by weight solution of potassium silanolate in xylene was added to this mixture with stirring, and this mixture was then purged with nitrogen gas in the flask. Additional catalyst was added to the mixture at room temperature to increase the viscosity of the reaction product until a target viscosity was obtained. When the reaction product viscosity reached a target viscosity, small pieces of dry ice were added to the flask to neutralize the basic catalyst. The neutralized salt was then removed through a pressure filter.

An amount of the above prepared reaction product was then added to 100 parts of the radiation curable coating delineated below. The radiation curable coating comprised 100 parts of a silicone vinyl ether copolymer, containing approximately 17% by weight of vinyl ether and having the general formula



wherein R denotes the group $-(\text{CH}_2)_2\text{Si}[\text{O}(\text{CH}_2)_4\text{OCH}=\text{CH}_2]_3$ and having a viscosity of 1200 mPa · s and 1 part of a tolyl (didodecylphenyl) iodonium trifluoromethanesulfonate (i.e. triflate) initiator. The curable coatings containing our reaction product were then tested for the amount of silicone mist generated off of a coater as described above. The results of this test are delineated in Table VI.

Table VI

Example	Reaction Product (parts per 100 parts of curable coating)	Total Mist (mg/m ³)	
		457.2 m/min.	609.6 m/min.
51	0	11.03	10.08
52	5	4.91	7.00
53	10	5.66	4.95

As seen from Table VI, the radiation curable coating compositions containing the reaction product of this invention had a significant reduction in the amount of mist coming off the coater during high speeds, in comparison to a radiation curable coating which does not contain this reaction product.

Examples 54-75

Into a 500 ml 3-neck flask were added 100 parts of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer, having a total average degree of polymerization of 12 and 50 mole percent of methylhydrogen moiety on the siloxane chain, .01 part of a dimethylvinylsiloxy-endblocked polydimethylsiloxane-polymethylperfluorobutylethylsiloxane-methylvinylsiloxane copolymer having a degree of polymerization of 300, and an amount of a glycol denoted in Table VII. Next, the mixture was heated to a temperature of from 120 to 130°C, and this temperature was maintained for 30 minutes. During this time, the mixture in the flask was stirred and purged with nitrogen gas. The reaction temperature was then cooled to room temperature. Then, .05 part of potassium silanolate (denoted "no solv" in Table VII) or 200 parts of toluene in 100 parts of the above mixture and then .05 part of potassium silanolate (denoted "toluene" in Table VII), were added to this mixture with stirring and this mixture was then purged with nitrogen gas in the flask. The type of catalyst employed is also denoted in Table VII. Additional catalyst was then added to the mixture at room temperature to increase the viscosity of the reaction product until a target viscosity was obtained. When the reaction product reached the target viscosity, small pieces of dry ice were added to the flask to neutralize the basic catalyst. The neutralized salt was then removed through a pressure filter and the solvent was stripped using a rotovap (when toluene was used as a solvent).

Thereafter, 1.5 parts of each of the above prepared reaction products were then added to 100 parts of a curable coating comprising 100 parts of an organopolysiloxane, having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeHexSiO})_b\text{SiMe}_2\text{Hex}$, wherein said organopolysiloxane has 2 mole percent hexenyl groups and an average degree of polymerization of 150. The curable coating, containing the above prepared reaction product of the instant invention, was then tested for the amount of silicone mist generated off a coater as described above. As a comparison, the amount of mist generated by the curable coating above without the reaction product of this invention was also measured. This latter result is denoted in Table I as the Comparison (Comp.) Coating. The results of this test are delineated in Table VII. In Table VII, PEG™ 600 denotes polyethylene glycol having a molecular weight of 600, PPG™ 1000 denotes polypropylene glycol having a molecular weight of 1000 and PPG™ 2000 denotes polypropylene glycol having a molecular weight of 2000.

Table VII

5	Catalyst Type Ex.	Total Mist (mg/m ³)					
		Glycol		457.2 m/min.		609.6 m/min.	
		Type	Amount (Parts)	Invention	Comp. Coating	Invention	Comp. Coating
10	54 toluene	PEG 600	10	1.83	1.28	6.23	4.91
15	55 toluene	PEG 600	6	0.74	---	2.21	---
20	56 toluene	PEG 600	8	1.07	---	2.34	---
25	57 toluene	PEG 600	10	0.39	1.28	0.83	4.91
30	58 toluene	PEG 600	15	0.49	1.28	2.14	4.91
35	59 no solv	PPG 1000	5	0.39	1.87	1.50	4.91
40	60 no solv	PPG 1000	10	0.79	1.45	2.17	4.77
54	61 no solv	PPG 2000	8	0.02	0.37	0.17	2.00
55	62 no solv	PPG 2000	10	0.58	2.55	2.77	6.43
56	63 no solv	PPG 2000	10	0.33	2.55	0.88	6.43
57	64 no solv	PPG 2000	10	0.15	1.48	0.51	4.46
58	65 no solv	PPG 2000	10	0.13	1.87	0.20	4.91
59	66 no solv	PPG 2000	10	0.13	2.55	0.15	6.43
60	67 no solv	PPG 2000	10	0.13	1.48	0.32	4.46
61	68 no solv	PPG 2000	10	0.19	2.55	0.27	6.43
62	69 no solv	PPG 2000	10	0.19	1.48	0.27	4.46
63	70 no solv	PPG 2000	15	0.33	1.28	0.38	4.91
64	71 no solv	PPG 2000	20	0.25	1.45	0.62	4.77
65	72 no solv	PPG 2000	20	0.26	1.45	0.71	4.77
66	73 no solv	PPG 2000	43	0.92	3.68	4.45	7.02
67	74 no solv	PPG 2000	59	0.24	1.48	1.27	4.46
68	75 no solv	PPG 2000	60	0.68	1.48	4.62	4.46

As seen from Table VII, curable coating compositions, containing the reaction product of the instant invention, had consistently lower misting values when compared to curable coatings which do not contain these reaction products.

Examples 76-79

The cure rate of a silicone coating is measured by determining the time to reach the state of No smear, No migration and No rub-off (NNN time). A cured coating is therein subjected to a finger rubbing test for No rub-off and No smear time. At a testing temperature, the silicone coating is allowed to cure for a certain period time with a 5 second increment for each period. Then, the coating surface is rubbed by a pointing finger several times. When the coating surface is free from finger trace, the coating reaches the No smear state. When the cured coating stays on the substrate securely without rubbing off, the No rub-off condition is achieved. Next, a strip of standard pressure sensitive testing tape is pressed down on the cured coating and then it is gently released. This is followed by allowing both ends of the adhesive strip to adhere together along its sticky surface and by then peeling the strip at a constant speed. If silicone migration exists on the adhesive surface, the two ends of the tape will pull off each other. When the coating reaches No migration, the two sides of sticky adhesive will stick together and the stuck line will continuously travel down as the peeling proceeds. In this example, the NNN times at various temperatures were recorded as a measure of substrate anchorage. The

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coating formulations without our additive did obtain No smear and No migration but they did not achieve the No rub-off condition. This is indicated as "nca" (no cure achieved) in Table IX.

An additional aerosol suppressant composition was prepared according to the procedure outlined in Examples 46-50.

An amount (shown in Table VIII) of the above prepared aerosol suppressant, was then added to 10 parts of a curable coating, comprising 97 parts of an organopolysiloxane having the general formula $\text{HexMe}_2\text{SiO}(\text{Me}_2\text{SiO})_a(\text{MeHexSiO})_b\text{SiMe}_2\text{Hex}$ wherein said organopolysiloxane has 2 mole percent of hexenyl groups and an average degree of polymerization of 150, 1.8 parts of a platinum catalyst (a soluble platinum complex containing 0.67% platinum formed from chloroplatinic acid and divinyltetramethyldisiloxane), 0.95 part of diethyl fumarate, 0.4 part of benzyl alcohol, and an amount (denoted in Table VIII) of a trimethylsiloxy-endblocked-polydimethylsiloxane-methylhydrogensiloxane copolymer having a total average degree of polymerization of 40 and 70 mole percent of methylhydrogen moiety on the siloxane chain. As a comparison, a curable coating composition which did not contain our aerosol suppressant composition was also prepared (denoted Comparison Example).

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Table VIII

Composition	Comparison Example	Example			
		76	77	78	79
Crosslinker (parts)	0.42	0.32	0.28	0.23	0.21
Suppressant (parts)	0	0.07	0.1	0.14	0.15

25 The curable coating compositions prepared above (Comparison Example and Examples 76-79) were then tested for cure time (seconds) to No smear, No migration and No rub-off (NNN time) as described above, on Mylar™ and biaxially oriented polypropylene film (BOPP) substrates, at various cure temperatures. The results are given in Table IX.

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Table IX

5	Composition	cure temperature (°C)	Substrate	Cure Time (sec. to NNN)
10	Comparison Example	82.2	Mylar Film	nca*
		87.3	Mylar Film	nca*
		93.3	Mylar Film	nca*
		104.4	Mylar Film	nca*
		148.9	Mylar Film	nca*
		82.2	Mylar Film	70
15	Example 76	87.3	Mylar Film	50
		93.3	Mylar Film	-
		104.4	Mylar Film	-
		148.9	Mylar Film	-
		82.2	Mylar Film	10
		87.3	Mylar Film	5
20	Example 77	93.3	Mylar Film	<5
		104.4	Mylar Film	<5
		148.9	Mylar Film	<5
		82.2	Mylar Film	5
		87.3	Mylar Film	<5
		93.3	Mylar Film	<5
25	Example 78	104.4	Mylar Film	<5
		148.9	Mylar Film	<5
		82.2	Mylar Film	5
		87.3	Mylar Film	<5
		93.3	Mylar Film	<5
		104.4	Mylar Film	<5
30	Comparison Example	148.9	Mylar Film	<5
		82.2	BOPP Film	nca*
		87.3	BOPP Film	nca*
		93.3	BOPP Film	nca*
		104.4	BOPP Film	nca*
		148.9	BOPP Film	nca*
35	Example 77	82.2	BOPP Film	-
		87.3	BOPP Film	-
		93.3	BOPP Film	5
		104.4	BOPP Film	<5
		148.9	BOPP Film	<5
		82.2	BOPP Film	-
40	Example 79	87.3	BOPP Film	-
		93.3	BOPP Film	5
		104.4	BOPP Film	<5
		148.9	BOPP Film	5

* Mylar™ is a trademark of E. I. duPont de Nemours and Company for polyester films.

** nca=indicates no cure achieved (i.e. there was ruboff).

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50 Claims

1. A method of making an aerosol suppressant composition, the method comprising the steps of:

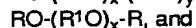
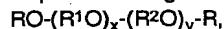
(I) reacting a mixture of:

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(A) an organosilicon compound selected from the group consisting of (i) an organohydrogensilicon compound, (ii) an organosilicon compound having in the compound at least one group selected from the group consisting of olefinic hydrocarbon radicals having from 2 to 14 carbon atoms, vinyl ether groups, epoxy

groups, amine groups, hydroxyl groups, alkoxy groups, carboxyl groups, isocyanate groups, oxime groups, acetoxy groups, and mixtures thereof, and (iii) mixtures of (i) and (ii);

(B) a compound having its formula selected from the group consisting of:

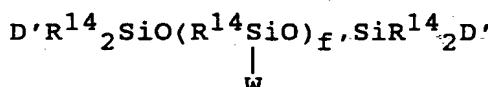
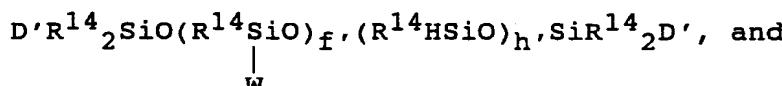
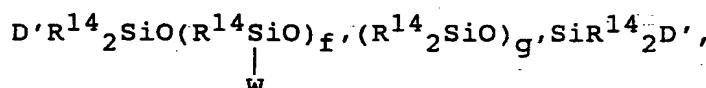
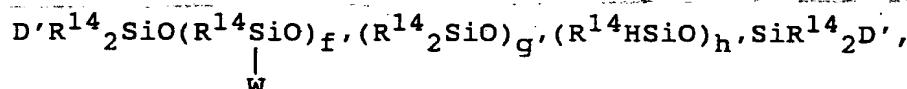


wherein R is selected from hydrogen atom or an olefinic hydrocarbon radical having from 3 to 14 carbon atoms, R¹ and R² are alkylene radicals having from 2 to 4 carbon atoms with the proviso that R¹ and R² are not the same alkylene radical at any given time, x has a value of from 1 to 200, y has a value of from 1 to 200, with the proviso that R is the same on both molecular chain ends;

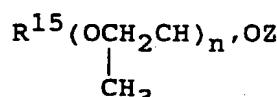
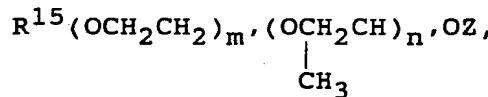
10 (C) a catalyst selected from metal catalysts or complexes of metal catalysts; and

(D) a monohydric alcohol having from 1 to 30 carbon atoms and containing olefinic unsaturation to form a reaction product.

15 2. A method according to claim 1 wherein the method further comprises adding, after step (I), a silicone glycol copolymer having its general formula selected from the group consisting of



wherein R¹⁴ is a monovalent hydrocarbon radical having from 1 to 10 carbon atoms, D' is R¹⁴ or W, f has a value of 1 to 20, g has a value of 1 to 200, h has a value of 1 to 200, W is a polyoxyalkylene group having its average structure selected from



55 wherein R¹⁵ is selected from a divalent hydrocarbon group having 1 to 20 carbon atoms or a urethane group, m has a value of 1 to 50, n has a value of 1 to 50, and Z is selected from the group consisting of hydrogen atom, an alkyl radical having 1 to 6 carbon atoms and an acyl group having 2 to 6 carbon atoms with the proviso that the value of m+n is greater than 5.

3. A method according to claim 2 wherein the method further comprises heating the mixture of (I).
4. A method of making a curable silicone coating composition comprising adding the aerosol suppressant composition of claim 1 to a curable composition comprising:
 - (i) an organosilicon compound having at least two groups selected from olefinic hydrocarbon radicals having from 2 to 14 carbon atoms or hydroxyl groups;
 - (ii) an organohydrogen/silicon crosslinking agent;
 - (iii) a metal catalyst; and
 - (iv) an inhibitor.
5. A method according to claim 4 wherein the curable silicone coating composition further comprises a high release additive.
6. A method according to claim 4 wherein said curable silicone coating composition further comprises a solvent.
7. A method according to claim 4 wherein said curable composition comprises:
 - (i) an organosilicon compound having at least two groups selected from the group consisting of epoxy groups, vinyl ether groups, acrylate groups, acrylamide groups, and olefinic hydrocarbon radicals having from 2 to 14 carbon atoms; and
 - (ii) an initiator.
8. A method of suppressing mist in a curable silicone coating composition comprising adding the composition obtainable by the methods of claims 4 or 7 to the curable silicone coating composition.
9. A method of claim 8 characterized in that said obtainable composition has a surface tension of greater than or equal to 25 dynes per centimeter.
10. A method of making a cured coating, the method comprising the steps of:
 - (I) coating the curable silicone coating compositions of claims 4 or 7 on the surface of a substrate;
 - (II) exposing said coating and substrate to atmospheric moisture or an energy source selected from (i) heat or (ii) actinic radiation in an amount sufficient to cure the coating.
11. A method according to claim 10 wherein the method further comprises applying a pressure sensitive adhesive on the coating after step (II).
12. A method of improving the anchorage of a curable silicone coating composition to a substrate, comprising adding the aerosol suppressant composition of claim 1 to a curable composition and then applying and curing the curable coating composition on said substrate.

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